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New application

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**Method and slip for making a shaped body out of ceramic material, ceramic shaped body and use of such a shaped body**

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Description:

The invention relates to a method of making a shaped body out of ceramic material and a slip for making such a shaped body. In addition, the invention relates to a ceramic shaped body and the use of such a ceramic shaped body.

5 In principle, two methods are known for making sintered ceramic shaped bodies.

First of all, it is known to press powder into the desired shape and to sinter the pressed green product so obtained in order to make the ceramic product. One disadvantage is that only limited shapes are possible. In addition, the green product  
10 shrinks during the sintering process. For this reason, a method is disclosed in EP 0 413 456 B1 according to which the ceramic powder containing silicon carbide (SiC) is suspended in ethanol, ground finer if necessary, and sifted. Afterwards, the ethanol is expelled and the powder so obtained is pressed into a green product and subsequently sintered under an oxygen atmosphere. The silicon carbide oxidises  
15 into silicon oxide (SiO<sub>2</sub>) in the process and counteracts the shrinkage.

Secondly, it is known to make a slip from ceramic powder. In the process, the ceramic powder is suspended in a solvent, usually water, together with a polymeric binder. The slip is poured into a mould and then consolidated, in the course of which  
20 a sol-gel transition occurs and a solid body forms. This body can be removed from the mould without changing its shape. The body is dried, and the actual green product forms in the process, shrinking sharply as it does so. In order to reduce dry shrinkage during drying, it is freeze-dried, supercritically (under pressure) or dried under a vacuum. The freeze-drying is often carried out under a simultaneous  
25 vacuum. The green product can then be sintered, in the course of which the binder escapes. One advantage of this process, which is known as gel-casting, is that very

complex shapes can be formed. A disadvantage, however, is that the sintered shaped body shrinks considerably compared to the cast and green product.

5 Experiments have been carried out in order to minimise the shrinkage in ceramics cast from a slip. From EP 1 122 227 A2, for example, it is known to add silicon or a mixture of aluminium and aluminium oxide to the slip. After consolidation and freeze-drying, the green product obtained in this way is sintered under an oxygen atmosphere. The dimensional stability is still unsatisfactory with this process.

10 Proceeding from this, the problem on which the invention is based is to provide a method of making ceramic shaped bodies which uses the advantages of gel-casting, in order to be able to model complex shapes as well, and in which a controlled volume change is possible at the same time, while avoiding the complex drying processes of gel-casting. Another problem on which the invention is based is to  
15 provide a slip and a shaped body of this kind. Finally, advantageous uses for ceramic shaped bodies produced in this way will be indicated.

In order to solve this problem, a metal oxide powder and a metal powder are, in accordance with the method of the invention, stirred in a colloidal sol into slip and  
20 that slip is then consolidated in a mould into a green product, and finally the green product is sintered in an active atmosphere which enables the metal powder to oxidise, to form the shaped body.

A central feature of the invention is that the slip manages without a binder. The gel-  
25 like green product arises solely as a result of the consolidation of the slip after it is poured into the mould. Specifically, the slip is cooled down in the mould in the process to a temperature lower than the freezing point of the solvent for consolidation purposes, which may be described as freeze-gelling. What is surprising about this is that, even after the solvent has been thawed, the body  
30 retains its shape without changing its contours. The green product is now dried. Since the green product already has a solid shape, this can be done under normal conditions or, in order to accelerate the drying process, at an elevated temperature. The green product retains the contours of its shape while drying. Complex drying methods, such as with gel-casting as described above, are not necessary. The  
35 green product is sintered under an atmosphere which enables the metal powder to oxidise, preferably an oxygen atmosphere. Because of the open porosity of the green product, the oxidising agent, i.e. preferably the oxygen, penetrates into the green product, so that the metal powder oxidises. According to the method of the invention, something takes place which might be described as reaction sintering.  
40 The invention is based on the finding that shrinkage can be reduced firstly by avoiding the use of the binder. Secondly, shrinkage is compensated by the oxidation

of the metal powder. In this context, by selecting the appropriate quantity of powder, the degree of shrinkage can be adjusted to a desired amount, which also includes zero shrinkage, or even over-compensated. Furthermore, it has been found that the ceramic obtained in this way exhibits improved mechanical properties compared to classic gel-casting. Even the green product possesses enhanced strength.

In order to improve the mechanical properties still further, especially tensile strength and impact value, a reinforcement of ceramic fibres, such as oxide, carbide and/or nitride fibres, can be added to the slip. In order to obtain a thermally or electrically conductive ceramic, a conductive material, such as silicon carbide, can also be added to the slip. Finally the slip can also be doped with carbon or carbon fibres. The carbon is burned completely during sintering, leaving behind deliberately introduced pores and/or channels in the shaped body.

Furthermore, in accordance with a further embodiment of the invention, the surface characteristics of the ceramic shaped body can also be influenced during the production process. It is, for example, possible subsequently to infiltrate a substance into the green product which determines the surface characteristics of the later shaped body. Silanes, siloxanes, sols, a metal melt, a glass melt and/or a slip are conceivable here. Alternatively the substance can also be subsequently infiltrated into the finished ceramic.

In order to solve the problem, the slip of the invention consists of a mixture of metal oxide powder and metal powder suspended in a colloidal sol. This slip can be sintered according to the method described above. Suitable sols are in particular silicon dioxide sol (silica sol), aluminium oxide sol, aluminium hydroxide sol (boehmite) and/or zirconium oxide sol. These ought to be present in the form of a nanosol. Suitable metal oxides are in particular silicon, aluminium, zirconium, titanium, calcium, magnesium oxide and/or mullite and/or spinel. for the metal powder, it is possible to use precious, semi-precious or base metals and, alternatively, alloys of these metals or intermetallic alloys.

A ceramic shaped body which solves the problem on which the invention is based is produced by reaction-sintering, under an oxidising atmosphere, a green product made from a freeze-gelled slip prepared from a mixture of metal powder and metal oxide powder suspended in a colloidal sol.

Thanks to the very precise moulding accuracy and contour retention, a ceramic shaped body of this kind can preferably be used in advantageously in aerospace engineering, microsystems engineering, refractory engineering and/or casting, especially in casting moulds. The ceramic shaped body of the invention is

particularly advantageous for metal casting. It is, for example, possible in this way to produce a master pattern on a precise 1:1 scale and then to take a mould of it with the slip of the invention. In the process, precisely the amount of metal powder is added to the slip to ensure that the increase in volume during sintering corresponds exactly to the shrinkage of the later cast metal body. As a casting mould, therefore, the ceramic shaped body is then bigger to precisely the extent of the shrinkage of the metal casting. The invention can therefore be used particularly well for high-precision casting (high-precision moulding).

A further use can be found in the field of chromatography. It is known to use charges of ceramic powder in this field. From the above description it becomes clear that not only the degree of volume change (increase and decrease in volume and complete compensation), but also the porosity can be adjusted. This can be advantageously used to produce a monolithic ceramic shaped body with a reactive surface, such as for biotechnology, especially for chromatography.

In addition, the invention can be used very well in order to produce a composite component from a ceramic shaped body and a substrate. Ceramic components are very difficult to combine with other materials, such as metals. Thanks to the method of the invention, it is now possible to adjust that degree of volume change during sintering by adding the corresponding amount of metal powder to the slip in such a way that the ceramic shaped body is press fitted with the substrate.

The invention will now be explained in more detail with reference to an embodiment illustrated in the drawings.

Fig. 1 shows a flow chart of a method of making a ceramic shaped body with the features of the invention,

Fig. 2 shows a device for freeze-gelling a slip in a schematic representation,

Fig. 3 shows a scanning electron microscope image of a shaped body made by the method of the invention,

Fig. 4 shows a diagram of the shrinkage of ceramic materials made by the gel-casting process plotted against the sintering temperature compared to shaped bodies produced by the method of the invention,

Fig. 5 shows a possible application for a ceramic shaped body of the invention.

According to the method of the invention, a metal oxide powder and a metal powder, such as aluminium oxide powder and aluminium powder, are mixed. This mixture is homogenised into a colloidal sol, in this case silica sol, and suspended into a slip. The slip is then poured into a negative mould for the later shaped body and cooled, with the mould, to a temperature lower than the freezing point of the solvent, i.e. frozen. The temperature here ought to be well below the freezing point. In the present case, the slip is cooled with the mould to between  $-5^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$ . As a result, the slip turns irreversibly into a solid gel (green product). This green product can now be removed from the mould and subsequently thawed.

The green product is dried under normal conditions or at an elevated temperature in an air kiln and sintered under an oxygen atmosphere. Because of the open porosity, the oxygen penetrates into the green product, and the metal powder oxidises. The ceramic shaped body forms.

Fig. 2 shows a device in which the slip can be freeze-gelled. The device has coolant supply lines 10 and coolant drainage lines 11 indicated schematically as arrows. The slip 12, optionally with the mould, is placed in a cooling jacket 13, which may also be the mould for pouring off the slip 12 itself. The coolant causes the slip 12 to freeze and gel. A suitable coolant, if the slip is to be frozen to about  $-40^{\circ}\text{C}$ , is ethanol. At lower temperatures, down to about  $-80^{\circ}\text{C}$ , dry ice is suitable. At even lower temperatures, liquid nitrogen is used. The temperature has an influence on the size of the crystals of frozen solvent, in this case water from the sol, and thus on the pore size.

An image of a fracture surface of the ceramic shaped body taken with a scanning electron microscope is shown in Fig. 3. The ceramic material (light) and the pores (dark) can clearly be seen.

Fig. 4 shows a comparison between the ceramic material made by the method of the invention and a material according to the state of the art. It can be seen that material according to the state of the art already undergoes slight shrinkage at  $1,000^{\circ}\text{C}$ . At  $1,400^{\circ}\text{C}$ , the shrinkage already amounts to about 10 %, while the material produced in accordance with the invention does not undergo any shrinkage.

According to a second embodiment, a metal oxide sol, such as silicon sol (silica sol), is stirred into a homogeneous slip with a ceramic powder, such as mullite and/or aluminium oxide for example. Specifically, 50 parts by weight of aqueous silicon sol (40 wt.-%  $\text{SiO}_2$  in 60 wt.-% water) with a particle size of 14 nm and 100 parts by weight of ceramic powder are blended. In addition, there are 15 parts by weight of

metal powder, namely aluminium powder or a powder of aluminium with 5 % magnesium (AlMg5).

5 The slip is poured into a mould and freeze-gelled at  $-40^{\circ}\text{C}$ . After removal from the mould, the green product is dried at about  $70^{\circ}\text{C}$  and sintered under an oxygen atmosphere at at least  $1,000^{\circ}\text{C}$ , especially  $1,400^{\circ}\text{C}$ . In the process, the metal powder oxidises.

10 If desired, it is also possible to add so much metal powder or so little oxygen that the metal does not oxidise completely. Some metal powder then remains in the ceramic shaped body, so that the latter is thermally and electrically conductive. The same effect can be achieved if the green product is sintered at a lower temperature or if the reaction is interrupted by terminating the sintering process prematurely.

15 Thanks to the great freedom of design with respect to the mould, a wide range of uses are possible. The ceramic shaped bodies may, for example, be used as casting moulds, in refractory engineering or microsystems engineering.

20 By doping the slip with carbon, it is possible deliberately to introduce small channels in the shaped body, so that it may, for example, be used as a heat exchanger. The carbon burns off completely during sintering and leaves behind the channels or also deliberately introduced pores. The carbon forms a core, as it were, or even a large number of (microscopically) small cores.

25 It becomes clear from the above description that not only the degree of volume change (increase and decrease in volume and complete compensation), but also the porosity can be adjusted. This can advantageously be used for chromatography.

30 A further use of the invention is shown in Fig. 5, in which a filter 14 made from of a ceramic produced in accordance with the invention is pressed into a retaining ring 15. For this purpose, the slip, to which so much metal powder has been added that the green product increases in volume during sintering, is poured into the retaining ring 15 and freeze-gelled between two plate coolers by analogy with the device of Fig. 2. After thawing and drying, the green product is sintered in the retaining ring  
35 15, in the process of which its volume increases in accordance with the amount of metal powder added. The ceramic filter 14 is pressed into the retaining ring in this way.

List of reference numerals:

- 10 Coolant supply line
- 11 Coolant drainage line
- 12 Slip
- 13 Cooling jacket
- 14 Filter
- 15 Retaining ring